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Disilanylphosphine and Disilylphosphine

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Disilanylphosphine, $Si_2H_5PH_2$, and disilylphosphine, $(SiH_3)_2PH$, have been prepared and identified by n.m.r. spectroscopy. Disilanylphosphine has been isolated and characterized by determination of its infrared spectrum, its vapor pressure, and the products of its hydrolysis and pyrolysis.

Introduction

Silylphosphine, SiH_3PH_2, was first prepared by the pyrolysis of a mixture of silane and phosphine.[1,2] Trisilylphosphine, $(SiH_3)_3P$, was prepared by the reaction between bromosilane and potassium dihydrogen phosphide.[3]

$$3SiH_3Br + 3KPH_2 \rightarrow (SiH_3)_3P + 2PH_3 + 3KBr$$

Both silylphosphine and a material of empirical composition Si_2PH_7 were detected in the products of the decomposition of a mixture of silane and phosphine in a silent electric discharge.[4] The compound Si_2PH_7 intrigued us because of the possibility of the existence of two structural isomers. The purpose of the present investigation was to prepare macroscopic amounts of the material and, if possible, to identify, separate, and characterize the isomers.

Experimental

A mixture of silane and phosphine in a mole ratio of 2:1 was circulated in a closed system through an ozonizer-type electric discharge tube at −78° followed by a trap at −95° (toluene slush) until practically all the reaction gases were consumed. A similar method had been used earlier for the preparation of higher silanes,[5,6] germanes,[7] and "mixed" (ternary) hydrides.[4,8] The products of the reaction were first subjected to fractional condensation in a series of traps at −63° (chloroform slush), −95° (toluene slush), −130° (*n*-pentane slush), and −196° (liquid nitrogen). The unreacted silane and phosphine condensed in the −196° trap, and disilane and silylphosphine condensed in the −130° trap. Diphosphine, trisilane, and part of the Si_2PH_7 condensed in the −95° trap. The trap at −63° contained the higher silanes, higher ternary hydrides, and the remainder of the Si_2PH_7. The condensate in the −95° trap was allowed to stand at room temperature for 1 week, during which time the diphosphine decomposed almost completely. After pumping out a little hydrogen which had formed, the mixture was fractionally condensed in a trap at −83° (ethyl acetate slush) followed by a trap at −196°. Phosphine, trisilane, and only a trace of Si_2PH_7 collected in the −196° trap. The proton n.m.r. spectrum of the material collected in the −83° trap showed clearly the presence of both $(SiH_3)_2PH$ and $Si_2H_5PH_2$ in approximately equal amounts, as well as some trisilane. The condensate in the −63° trap was passed through a −45° trap (chlorobenzene slush) in order to remove most of the higher molecular weight compounds from the Si_2PH_7. The Si_2PH_7-rich condensates were injected into a gas chromatographic column containing silicone oil on firebrick at 70°. We were never able to elute disilylphosphine from the column; we assume that it was thermally decomposed on the column. The observed presence of small amounts of phosphine and silylphosphine in all the elution fractions is consistent with this interpretation. The method of injecting the mixture in the chromatographic apparatus and of collecting the different fractions was similar to that used in the preparation of the tetrasilanes.[6] It was found that ordinary injection needles became clogged in spite of all reasonable precautions. Gas-tight syringes with Teflon-tipped plungers and 22- or 23-gauge needles were more satisfactory. When syringes with removable needles were used, a little grease had to be used at the joints to make them gas-tight. The chromatograms showed that the retention times of Si_3H_8 and $Si_2H_5PH_2$ were in the proportion of roughly 1:2. The peak of $Si_2H_5PH_2$ preceded the peaks of the tetrasilanes. It was found that the $SiH_3SiH_2PH_2$ was contaminated with a small amount of $(Si_2H_5)_2O$. By keeping the contaminated product in a trap at −78° and by pumping out the vapors into a trap at −196°, it was possible to recover pure disilanylphosphine. Starting with 250 mmoles of the SiH_4–PH_3 mixture, about 3 mmoles of $Si_2H_5PH_2$ was obtained.

The proton n.m.r. spectra were obtained with a Varian Associates A-60 n.m.r. spectrometer, and the infrared spectra with Perkin-Elmer Infracord spectrophotometers (NaCl Model 137B and KBr Model 137). The n.m.r. spectrum for pure liquid $SiH_3SiH_2PH_2$ is given in Fig. 1. Although $(SiH_3)_2PH$ was not obtained in pure form, the relevant portions of the spectrum of a mixture containing about 30% $(SiH_3)_2PH$ are given in Fig. 2 and 3. The infrared spectrum of disilanyl phosphine shows absorptions, as seen in Fig. 4, at the following frequencies (cm.$^{-1}$): 2300 (w), 2150 (s), 1070 (sh, w), 990 (w), 942 (m), 932 (m), 888 (s), 877 (s), 790 (sh, s), 784 (s), 736 (w), 728 (w), 724 (w), 637 (w), 628 (w), and 475 to 515 (w, br).

The vapor pressure of disilanylphosphine was found to be 31 ± 1 mm. at 0° and 81 ± 1 mm. at 20°. It was found during the fractional condensation that the isomers $(SiH_3)_2PH$ and $Si_2H_5PH_2$ could not be separated from each other even partially. Thus we conclude that the volatilities of the two isomers are very similar. Gas-density molecular weights of 92.1, 95.5, and 96.0 were obtained for three different samples at room temperature (calculated for Si_2PH_7: 94.2). The mass spectrum of disilanylphosphine showed bands corresponding to the fragments Si_2P^+–$Si_2PH_7^+$, Si_2^+–$Si_2H_6^+$, SiP^+–$SiPH_5^+$ (uncertain because of ambiguity with $Si_2H_x^+$), Si^+–SiH_4^+, and P^+–PH_3^+.

In several experiments, $Si_2H_5PH_2$ vapor was allowed to remain in contact with an excess of water vapor for several hours. Analysis showed that the main hydrolysis products were phosphine and bisdisilanyl oxide, and that very small amounts of disilane and silane were formed. The glass walls of the reaction tubes became coated with a very thin white deposit. In one experiment 0.204 mmole of $Si_2H_5PH_2$ and 0.147 mmole of H_2O were allowed to react for 4 hr. at room temperature, yielding 0.208 mmole of PH_3, 0.126 mmole of a mixture of H_2O and $(Si_2H_5)_2O$ (it was not possible to separate these two), and a trace of Si_2H_6 and SiH_4. The products were identified by their infrared spectra.

Traces of phosphine and disilane were formed when disilanyl-

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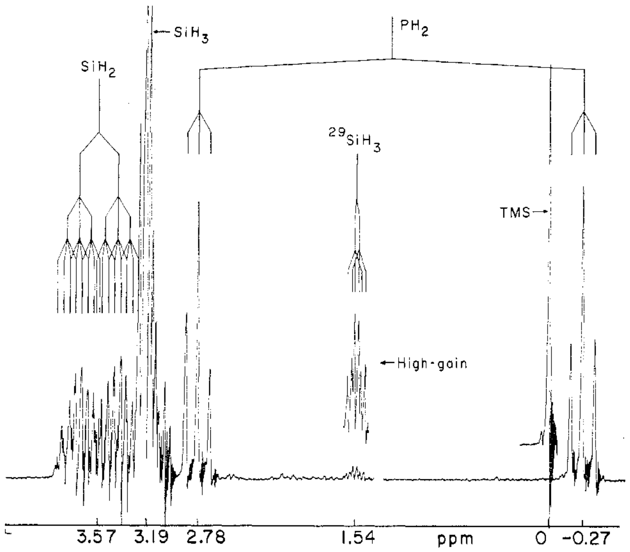

Fig. 1.—N.m.r. spectrum of disilanylphosphine at 60 Mc. Chemical shifts to low field of external TMS.

phosphine was stored for 1 day at room temperature while exposed to ordinary room light. When kept as the vapor in a sealed tube at either 50 or 110° for 1 day, about 5% of the compound decomposed to give phosphine and disilane. No other products were found. When kept at 210° for 1 day, 32% of the compound decomposed to give disilane, silylphosphine, and (by mass spectroscopy) Si_3PH_9 and possibly $Si_2P_2H_8$. No phosphine or hydrogen was found in the 210° pyrolysis. A faint solid film formed on the inner wall of the container.

Discussion

N.m.r. Spectra.—The chemical shift data are presented in Table I. When the proton n.m.r. spectrum of trisilane[9] is compared with that of disilanylphosphine (Fig. 1), it is noticed that the relative positions of the resonances due to the SiH_3 and SiH_2 groups are reversed.

Table I

Chemical Shifts to Lower Field of TMS in P.p.m. ±0.01

	$(SiH_3)_2PH$	$SiH_3SiH_2PH_2$
SiH_3	3.70	3.19
SiH_2		3.57
PH_2		1.25
PH	0.40	

It is tempting to suggest that the protons in the SiH_2 group of $SiH_3SiH_2PH_2$ are less shielded than those in the SiH_2 group of $SiH_3SiH_2SiH_3$ because phosphorus is more electronegative than silicon. Perhaps for the same reason, the protons of the SiH_3 group in $(SiH_3)_2PH$ are less shielded than those of the SiH_3 group in $SiH_3SiH_2PH_2$. Although we cannot explain the fact that the SiH_3 protons in trisilane are less shielded than those in disilanylphosphine, this datum is consistent with the observed variations of the chemical shift of the SiH_3 group in disilanyl halides[10] and the higher silanes.[9] The proton of the PH group in $(SiH_3)_2PH$ is more shielded than the protons of the PH_2 group in $Si_2H_5PH_2$, perhaps because silicon is less electronegative than hydrogen.

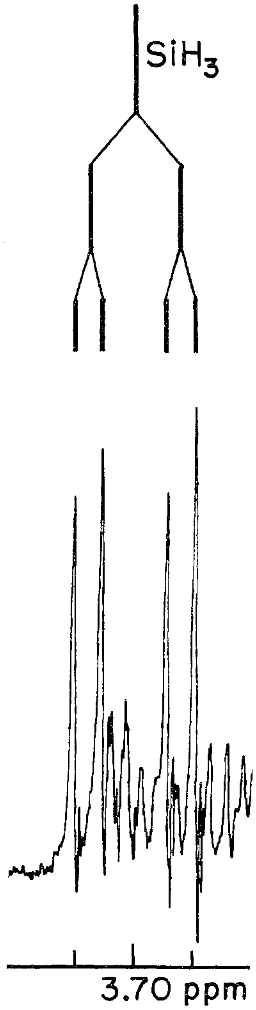

Fig. 2.—Portion of n.m.r. spectrum of disilylphosphine at 60 Mc. Chemical shift to low field of external TMS.

The coupling constant data are presented in Table II. The SiH_3 proton signal of $SiH_3SiH_2PH_2$ is split into a pair of triplets by the SiH_2 protons and the phosphorus atom. This pattern is not clearly observable in the main resonance, but the ^{29}Si satellite resonance on the high-field side of the main resonance very clearly shows this pattern when seen at high gain. The SiH_2 proton signal of $SiH_3SiH_2PH_2$ is split into a pair of triplets, each line of which is split into a quartet, by the phosphorus nucleus and the two other types of protons in the molecule. It happens that the $\overline{SiH_3SiH_2}$ coupling constant is approximately half of the $\overline{SiH_2PH_2}$ coupling constant; therefore there is a near-superposition of lines, as shown in Fig. 1, causing the signal to look something like a pair of octets. At lower sweep widths, the individual lines are resolved. The PH_2 proton signal of $SiH_3SiH_2PH_2$ is split into a pair of triplets by the phosphorus nucleus and the SiH_2 protons.

The SiH_3 proton signal of $(SiH_3)_2PH$ is split into a pair of doublets by the phosphorus atom and the PH proton. This spectrum is shown in Fig. 2, in which the weaker peaks are due to $Si_2H_5PH_2$ impurity. The PH

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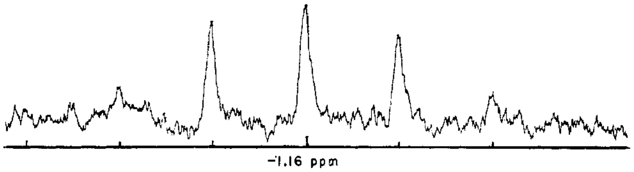

Fig. 3.—Portion of n.m.r. spectrum of disilylphosphine at 60 Mc. The septet of the PH proton on the high-field side of external TMS.

TABLE II
COUPLING CONSTANTS

J_{P-H}, c.p.s.

SiH_3PH	$-SiH_2PH_2$	$-SiH_2PH_2$
184.0 ± 0.5	182.5 ± 0.5	18.5 ± 0.2

$(SiH_3)_2PH$	$SiH_3SiH_2PH_2$
17.5 ± 0.2	2.0 ± 0.1

J_{H-H}, c.p.s.

$(SiH_3)_2PH$	$-SiH_2PH_2$	SiH_3SiH_2-
5.1 ± 0.1	5.8 ± 0.1	3.0 ± 0.1

proton signal of $(SiH_3)_2PH$ is split into a pair of septets by the phosphorus nucleus and the six SiH_3 protons. Because of this multiple splitting of a weak signal, the lines do not show up prominently. With very high gain, it is possible to see five of the peaks of each septet. The high-field multiplet is shown in Fig. 3. We observe an intensity ratio of 3.0:7.4:10:7.6:2.9, which corresponds much more closely to that expected for the middle five lines of a septet (3:7.5:10:7.5:3) than to that expected for a simple quintet (1.7:6.7:10:6.7:1.7).

The ^{31}P n.m.r. spectrum of $SiH_3SiH_2PH_2$ was observed to be a triplet of triplets, the splitting being due to the PH_2 and SiH_2 protons. The P–H coupling constants were, within experimental error, the same as those obtained from the proton n.m.r. spectrum.

Infrared Spectra.—The infrared spectrum of disilanylphosphine is presented in Fig. 4. The absorptions at 2300 and 2150 cm.$^{-1}$ can be easily assigned to the PH and SiH stretches, respectively. By comparing the spectrum with that of trisilane,[11] we tentatively assign the bands at 942 and 932 cm.$^{-1}$ and those at 888 and 878 cm.$^{-1}$ to the SiH_3 asymmetrical and symmetrical deformation modes, and the bands at 736, 728, and 724 cm.$^{-1}$ to SiH_3 wagging and SiH_2 bending modes. In their studies of the infrared spectra of diphosphine and silylphosphine, Nixon[12] and Linton and Nixon[13] assigned bands at 1081 and 1068.5 cm.$^{-1}$ to PH_2 deformation. Nixon assigned strong bands at 633 and 792 cm.$^{-1}$ in the spectrum of diphosphine to PH_2 wagging modes, and much weaker bands at 743 and 827 cm.$^{-1}$ to PH_2 twisting modes. We therefore suggest that the weak band at 1073 cm.$^{-1}$ in the spectrum of disilanylphosphine is due to PH_2 deformation, while the bands at 784 and 790 cm.$^{-1}$ and 637 and 628 cm.$^{-1}$ are due to PH_2 wagging and twisting. Linton and Nixon assigned the strong band at 454 cm.$^{-1}$ in the spectrum of SiH_3PH_2 to the Si–P stretch. In the case of SiH_3-SiH_2PH_2, a weak band is observed in the region of 515 to 475 cm.$^{-1}$ which could be due to the Si–P stretch.

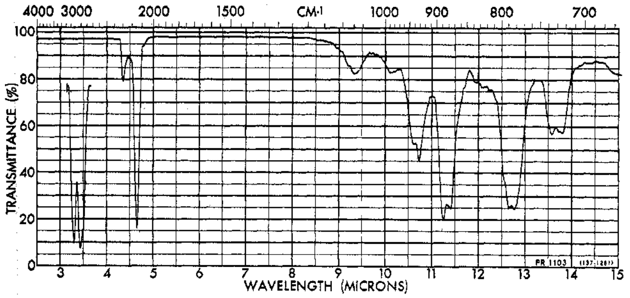

Fig. 4.—Infrared spectrum of disilanylphosphine (10 mm. pressure in 5-cm. cell). Lower curve at ∼3000 cm.$^{-1}$ is the polystyrene calibration. Weak bands at 825 and 838 cm.$^{-1}$ are due to impurities.

Reactions.—Disilanylphosphine reacts with an excess of water as follows.

$$2Si_2H_5PH_2 + H_2O \longrightarrow (Si_2H_5)_2O + 2PH_3$$

Thus the hydrolysis is analogous to the hydrolysis of disilanyl iodide, in which $(Si_2H_5)_2O$ and HI are formed.[14] Disilylphosphine is so unstable that it is completely decomposed on a chromatographic column at 70°, whereas disilanylphosphine is less than half decomposed after 1 day at 210°. Perhaps the instability of disilylphosphine is similar in cause to the presumed instability of disilylamine.[15]

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